Proceedings of the 3rd Annual Nitrogen: Minnesota's' Grand Challenge & Compelling Opportunity Conference

Thank you to all of our Supporters!

Minnesota Department of Agriculture

USDA

Minnesota Soybean Research & Promotion Council

Agrium

AgriGrowth

N-Serve Nitrogen Stabilizer

Dow AgroSciences Instinct HL Nitrogen Stabilizer

SMBSC

AGVISE Laboratories

MAWRC Minnesota Agricultural Water Resource Center

Minnesota Corn Growers Association

West Central

Koch Agronomic Services, LLC

MVTL

MNICCA

Nitrous Oxide Emissions from Fertilized Soil: Can We Manage It?

N_2O N_2O N_2O

Rodney T. Venterea

USDA-ARS St. Paul, MN

Dept. Soil, Water & Climate

University of Minnesota

venterea@umn.edu or rod.venterea@ars.usda.gov

USDA Agricultural Research Service

University of Minnesota Driven to Discover℠

2nd Annual NITROGEN: Minnesota's Grand Challenge
& Compelling Opportunity Conference
Mankato February 16

Technicians
Michael Dolan
Jason Leonard
Numerous summer technicians

Students and Post-docs
Martin Burger
Emerson Cordova
Ryo Fujinuma
Florence Sessoms
Bijesh Maharjan
Charles Hyatt
Erin Berryman
Adam Stanenas
Peter Turner

Collaborators
John Baker
Jeff Coulter
Fabian Fernández
Tim Griffis
Carl Rosen
Mike Sadowsky
Kurt Spokas
Jeff Strock

USDA ARS Agricultural Research Service
University of Minnesota Driven to Discover℠

Funding sources
-USDA-ARS
-Minnesota Corn Research & Promotion Council
-Minnesota Soybean Research & Promotion Council
-USDA-ARS Postdoctoral Associate Program
-Global Research Alliance
-Minn. Agricultural Fertilizer Research and Education Council
-NRI/USDA-CSREES Air Quality Program
-Agrium, Inc.
-Koch Agronomic Services
-John Deere

Outline

1. Background

- What is N_2O / Why it's important / How it is produced in soil

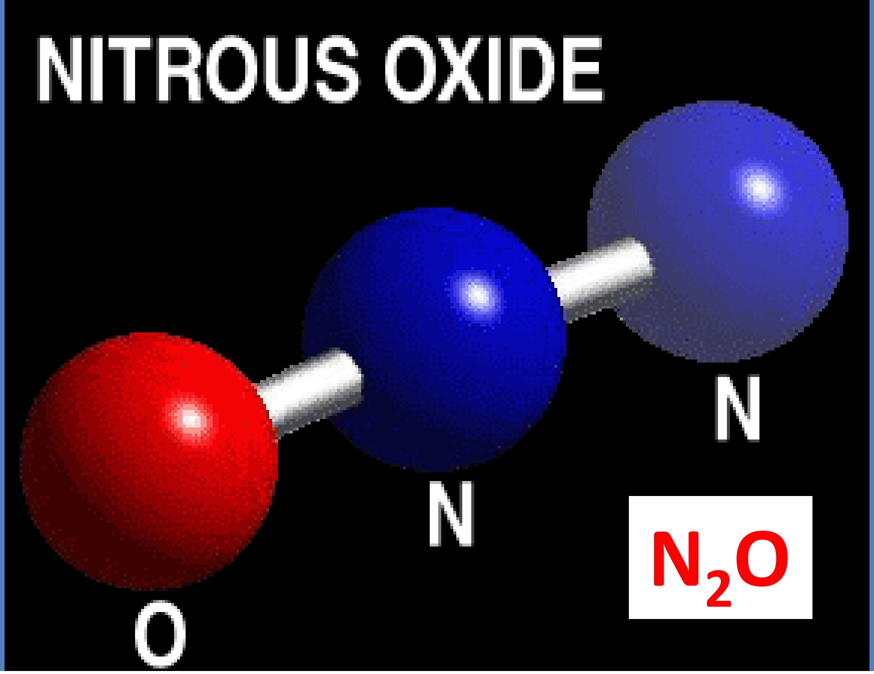
2. Challenges of reducing N_2O

- Unique aspects

3. Possible strategies for mitigation

- Summarize research findings (some counter-intuitive)

4. Connection to water quality issues



Boiling point	−88 °C
Molecular mass	44.01 g/mol (64% Nitrogen)
Solubility in water	1.5 g/L at 15 °C
Current atmospheric concentration	330 ppb

- **Manufactured for various uses:**

  Anesthetic, engine fuel, food propellant

- **By-product of biochemical processes in soil:**

  Nitrification, denitrification, chemo-denitrification

N_2O emissions from agriculture: Why is it important?

N_2O N_2O

<u>AGRONOMIC</u>

- **Usually NOT a large part of the N budget (< 1 to 5%)**
- **BUT: can be an indication of a 'leaky' system**

(i) The same soil processes that produce N_2O can also produce:

- **Dinitrogen (N_2) via DENITRIFICATION, and/or**
- **Nitric oxide (NO) via NITRIFICATION**
- **Together can account for 5 – 25% or more of applied N**

N_2O emissions from agriculture: Why is it important?

N_2O N_2O

AGRONOMIC

- Usually NOT a large part of the N budget (< 1 to 5%)
- BUT: can be an indication of a 'leaky' system

(ii) High N_2O emissions usually indicate high soil N levels:

- Nitrate (NO_3^-) → Leaching Losses
- Ammonium or ammonia (NH_3) → Volatilization Losses
- N_2O emissions can be a warning sign of high N losses via other pathways

N_2O emissions from agriculture: Why is it important?

N_2O N_2O

ENVIRONMENTAL

(i) N_2O depletes stratospheric ozone

- 1970s: Discovery that N_2O depletes ozone (P. Crutzen, Nobel Prize)
- Early measurements of N_2O from soil driven by this issue
- 1987: Montreal Protocol regulated CFCs but not N_2O
- Today: N_2O is most important ozone-depleting chemical being emitted *(Ravishankara et al. 2009)*

N_2O emissions from agriculture: Why is it important?

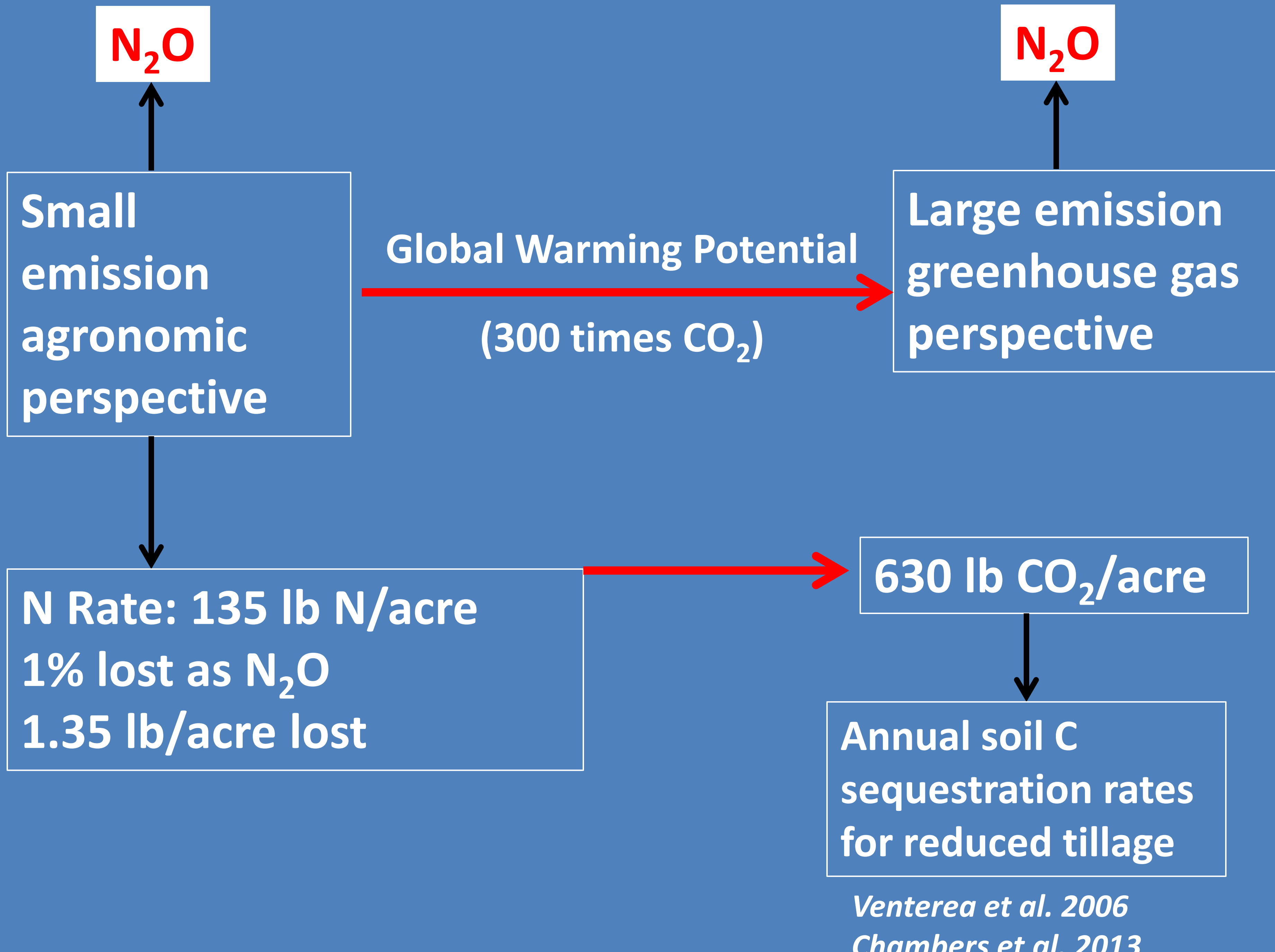
N_2O N_2O

<u>ENVIRONMENTAL</u>

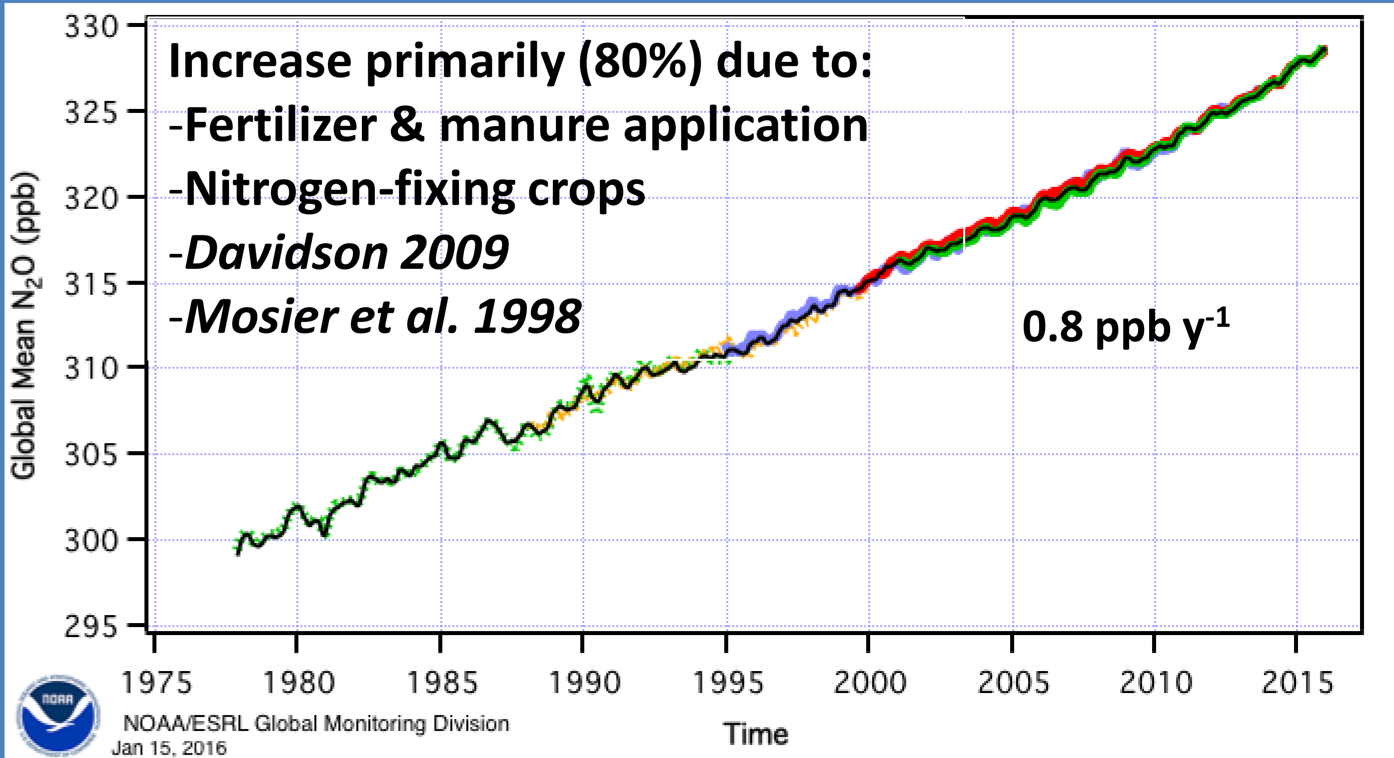
(ii) N_2O is a strong greenhouse gas

- **Absorbs IR radiation with a capacity 300 times greater than CO_2 (lb for lb)**
- **Global Warming Potential = 300**
  - **Long lifetime in atmosphere (> 100 years)**
  - **Molecular structure more efficient at absorbing IR radiation**

  (Forster et al., 2007)


N_2O
N_2O
Small emission agronomic perspective
Global Warming Potential
(300 times CO_2)
Large emission greenhouse gas perspective
N Rate: 135 lb N/acre
1% lost as N_2O
1.35 lb/acre lost
630 lb CO_2/acre
Annual soil C sequestration rates for reduced tillage
Venterea et al. 2006
Chambers et al. 2013

Changing N_2O in the atmosphere
Increased approx. 10% in past 40 years



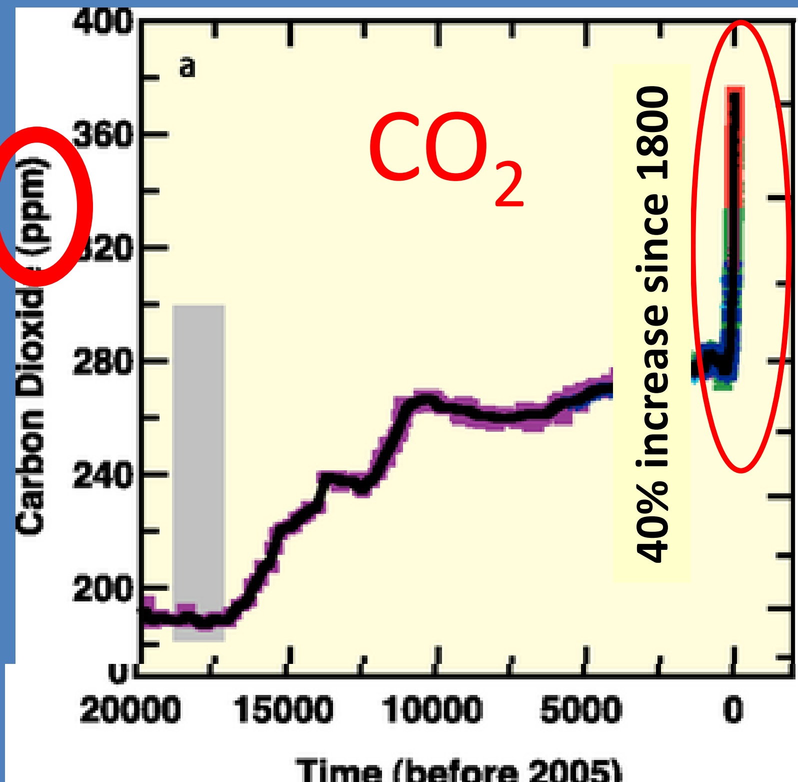
U.S. Department of Commerce / National Oceanic & Atmospheric Administration / NOAA Research

Earth System Research Laboratory
Global Monitoring Division

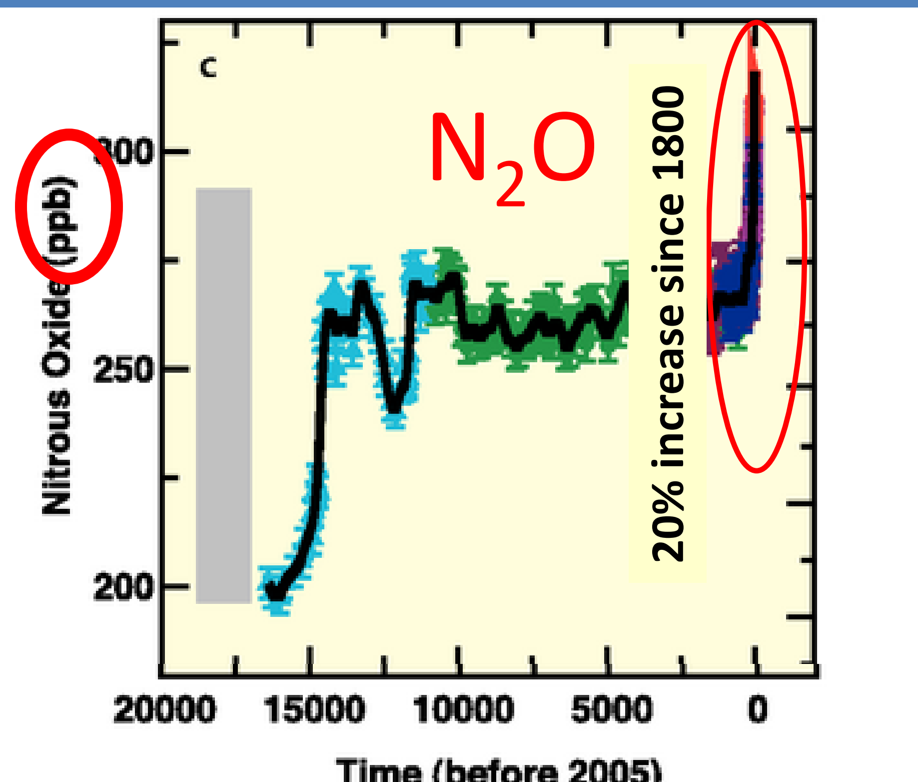
http://www.esrl.noaa.gov/gmd/hats/combined/N2O.html

Long-term changes in GHGs in the atmosphere
Ice Core Data

Atmospheric CO_2 concentration



Atmospheric N_2O concentration



ipcc INTERGOVERNMENTAL PANEL ON climate change WMO UNEP

https://www.ipcc.ch/publications_and_data/ar4/wg1/en/figure-ts-2.html

Long-term changes in N_2O in the atmosphere

High GWP + ppb concentration- Net Global Effect:

→ N_2O emissions account for 6.2% of total anthropogenic GHG emissions (IPCC)

http://www.ipcc.ch/pdf/assessment-report/ar5/syr/AR5_SYR_FINAL_SPM.pdf

U.S. Agriculture as a whole

→ N_2O emissions account for 55% of total GHG emissions (USEPA)

https://www3.epa.gov/climatechange/ghgemissions/usinventoryreport/archive.html

→ For intensively fertilized upland crops, N_2O can represent more than 60% of total GHG budget

e.g. *Jayasundara et al. 2014*

Potential Opportunities for Producers

Under carbon regulations currently in place in Alberta, Canada, farmers can earn 'Carbon offsets' for changing their mgmt practices in ways that reduce N_2O emissions "*through implementation of a 4-R (Right Source, Rate, Time and Place™) Nitrogen Stewardship Plan"*

http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/cl14145

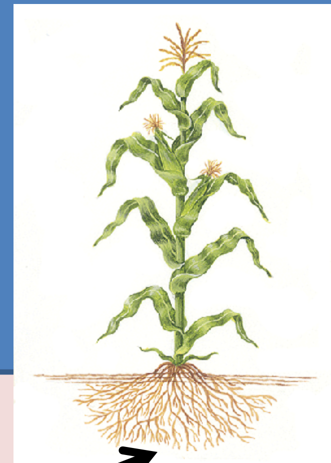
- **Could be win-win for farmers: Earn C credits + Reduce input costs**

Future of such programs uncertain in the U.S.
Similar plans under consideration in California - AB-32 legislation

https://www.arb.ca.gov/cc/ab32/ab32.htm

http://www.climateactionreserve.org/how/protocols/nitrogen-management/

N_2O Production in Soil



Nitrogen fertilizers (urea, AA etc)

Animal manures

Nitrogen Inputs to Soil

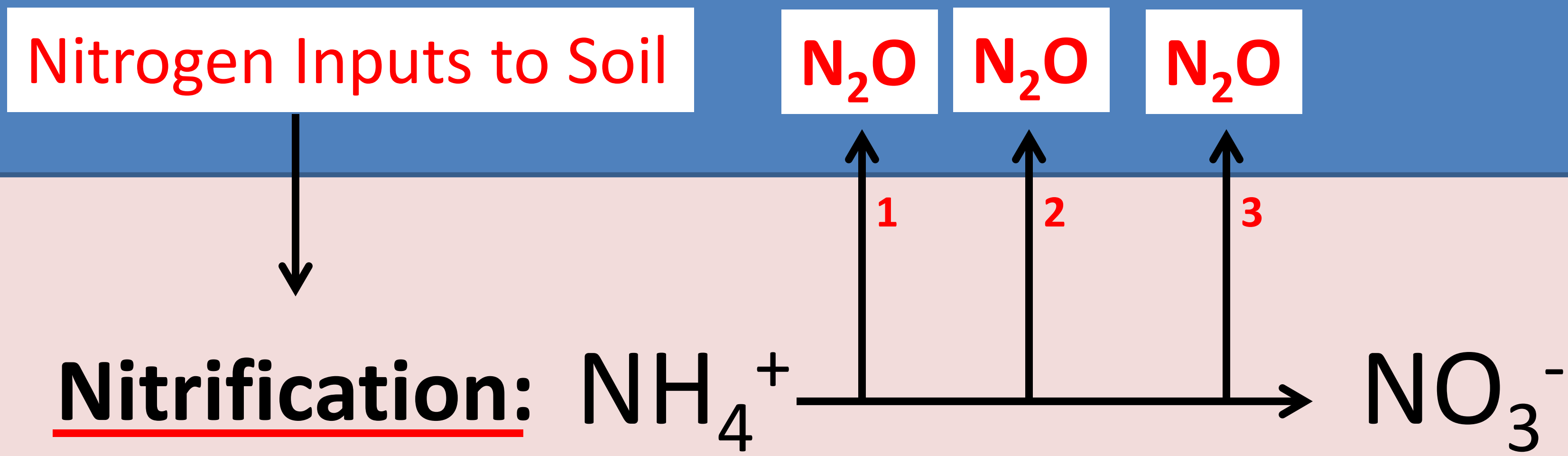
Nitrogen-fixation (e.g. soybean)

Mineralization of crop residues

N not used by plant

Stimulates Soil Processes

N_2O Production in Soil



1. Hydroxylamine oxidation
2. Biological nitrite reduction
3. Chemical nitrite reduction

Aerobic process:

Needs oxygen, moderate soil moisture

N_2O Production in Soil

Nitrogen Inputs to Soil

Denitrification: $N_2 \leftarrow NO_3^-$

N_2O (4)

4. Biological nitrate reduction

Anaerobic process:

Needs low / no oxygen and high soil moisture

Challenges of reducing N_2O emissions

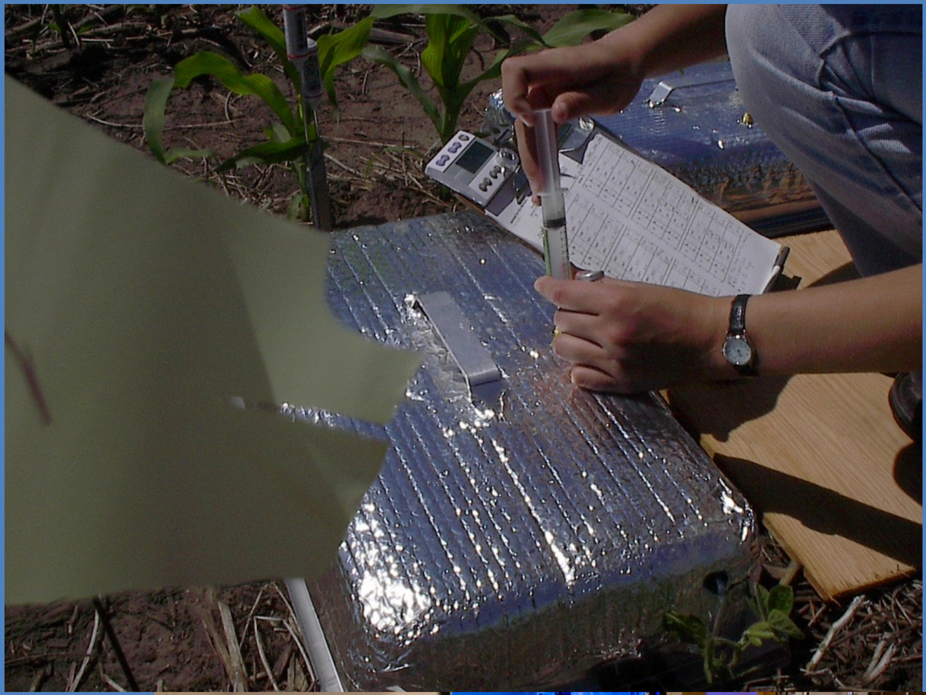
1. N_2O can be produced by several different biochemical reactions (4 or more) and under a wide range of conditions:

-Low to moderate soil moisture:
Nitrification → N_2O

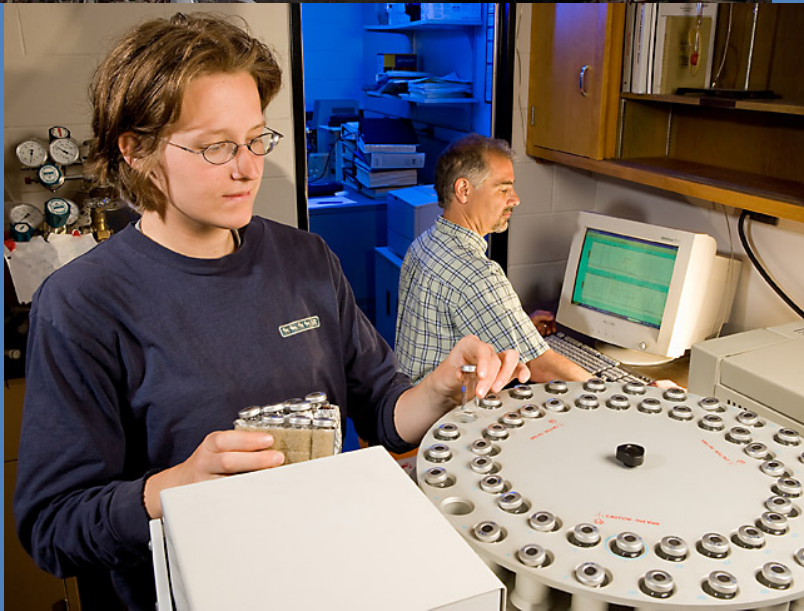
-High soil moisture:
Denitrification → N_2O

-Difficult/impossible to avoid such conditions if inorganic N is available in soil

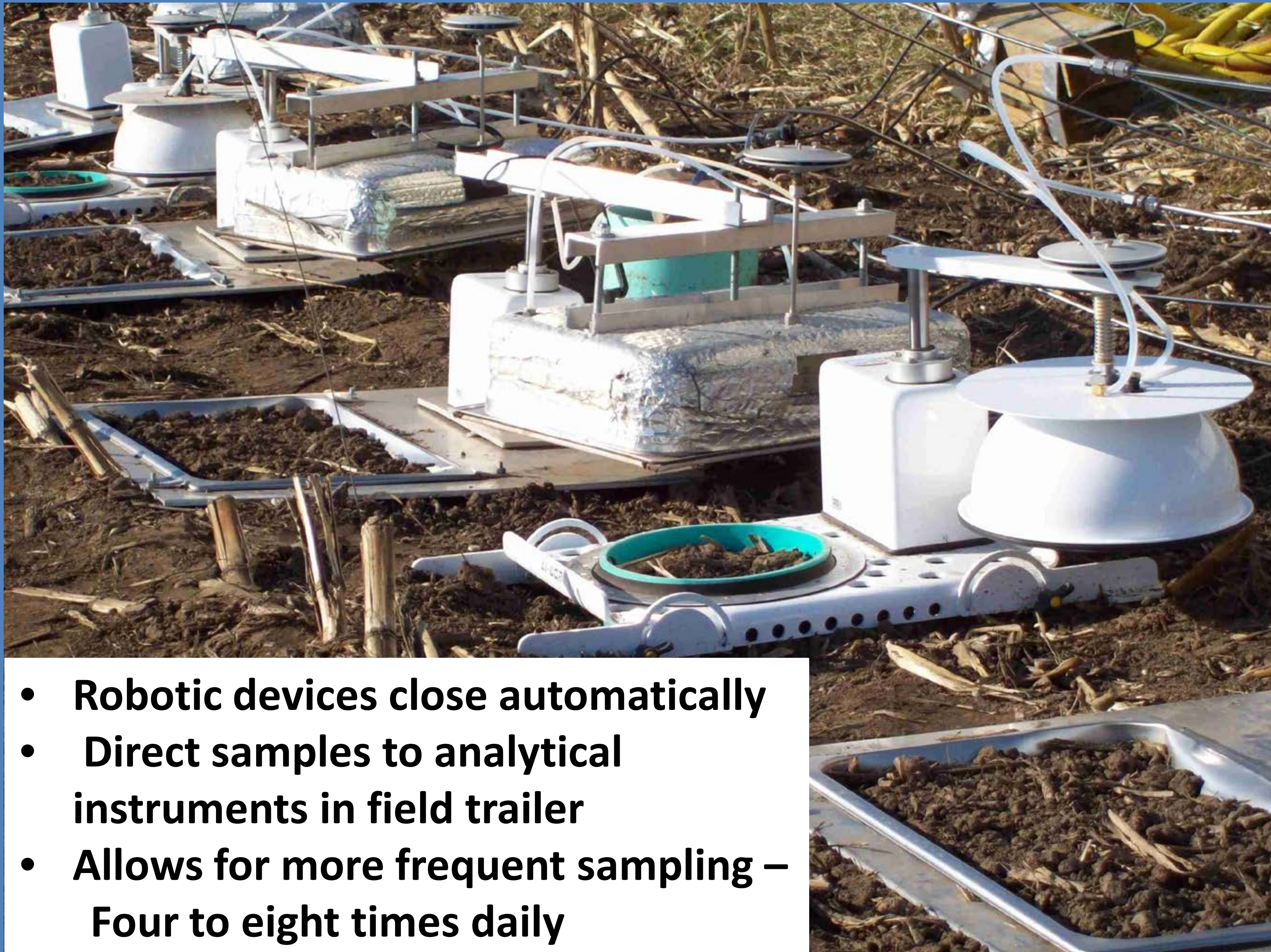
MANUAL CHAMBER MEASUREMENTS



- Open-bottom chambers on soil
- Samples collected by syringe
- Analyzed by gas chromatography
- Flux=rate of increase in concentration

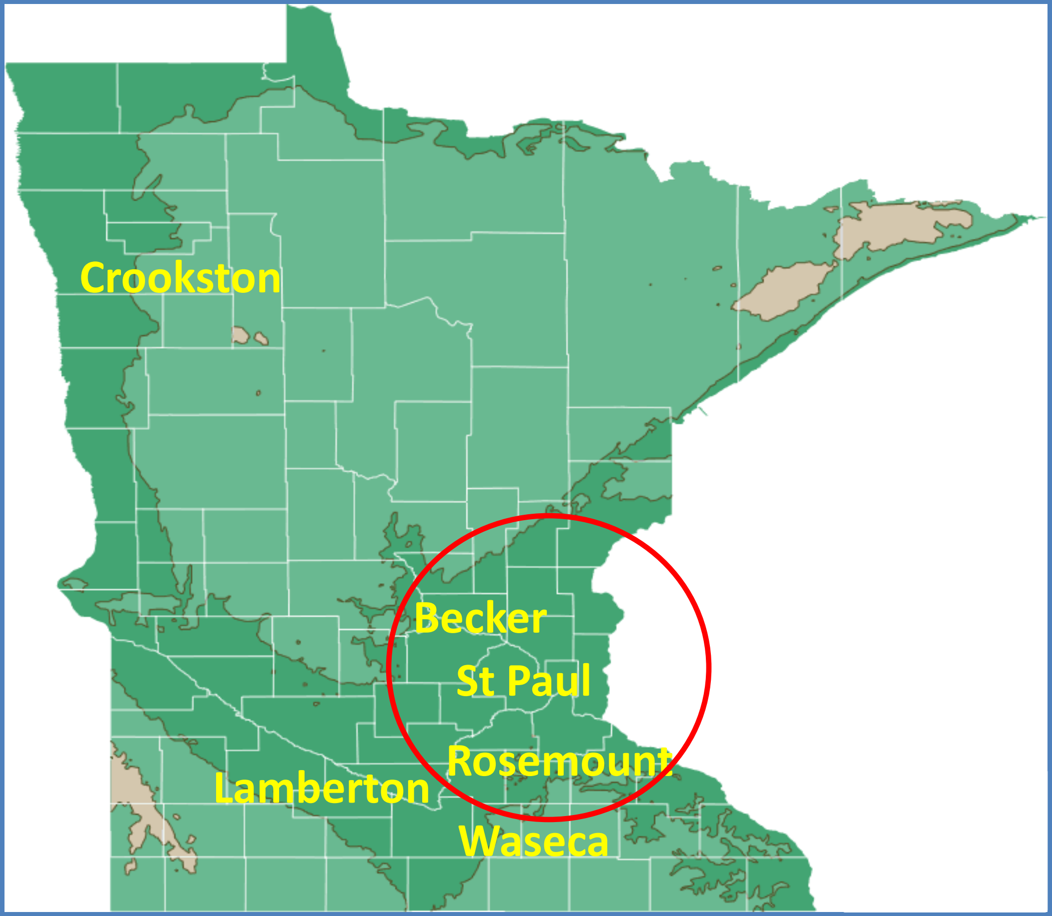


AUTOMATED CHAMBERS

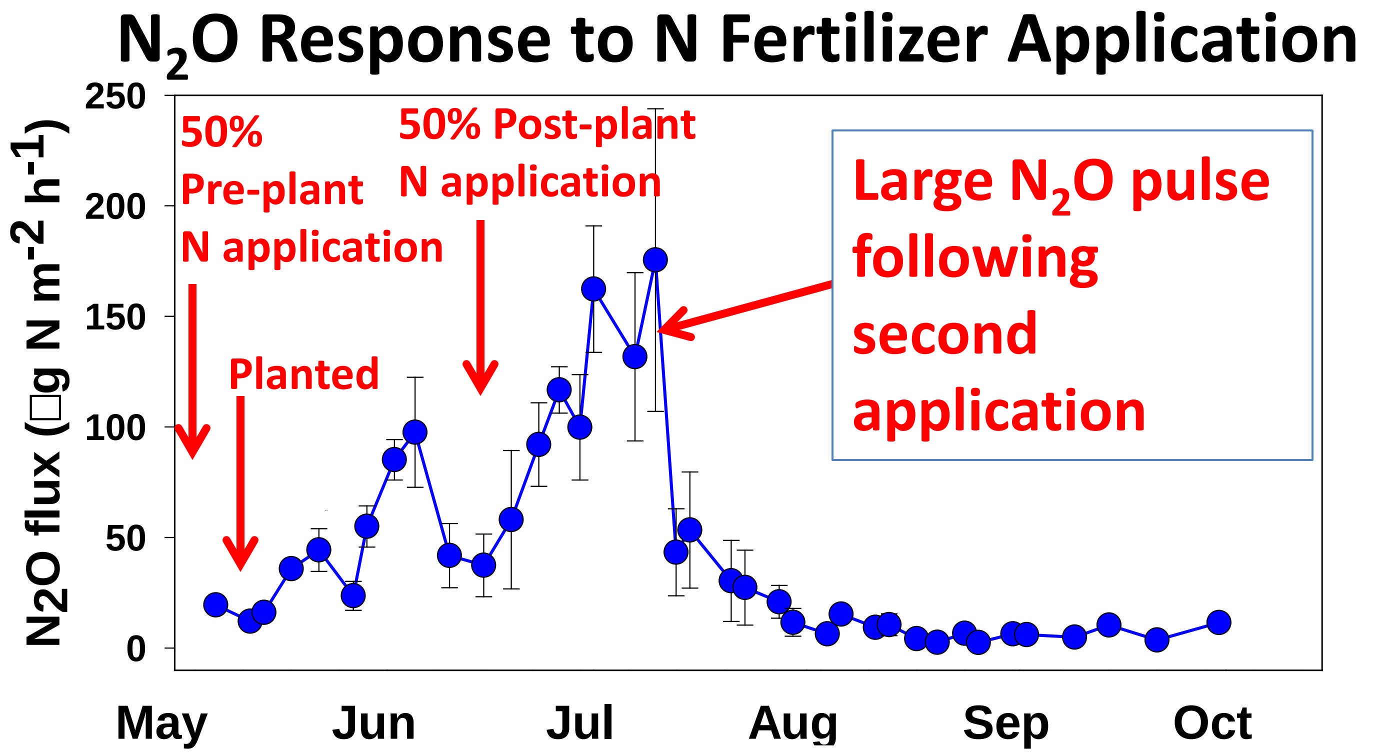


- Robotic devices close automatically
- Direct samples to analytical instruments in field trailer
- Allows for more frequent sampling – Four to eight times daily

FIELD SITES



CHAMBER MEASUREMENTS



Fujinuma et al. (2011)
Hubbard loamy sand
Becker, MN

Challenges of reducing N_2O emissions

2. **Large N_2O fluxes can occur even when the crop is present and well-developed**

-Soil biochemical reactions are very fast

-Diffusion of N_2O gas is very fast

-Higher temperatures later in season further speed up soil biochemical processes and diffusion

-Large precip events + warm temps → large fluxes

Can management be used to reduce N_2O emissions?

Basic Nitrogen Management Components (4Rs):

- Rate
- Source
- Placement
- Timing

Other Management Components:

- Tillage
- Rotation
- Residue mgmt
- Irrigation
- Drainage

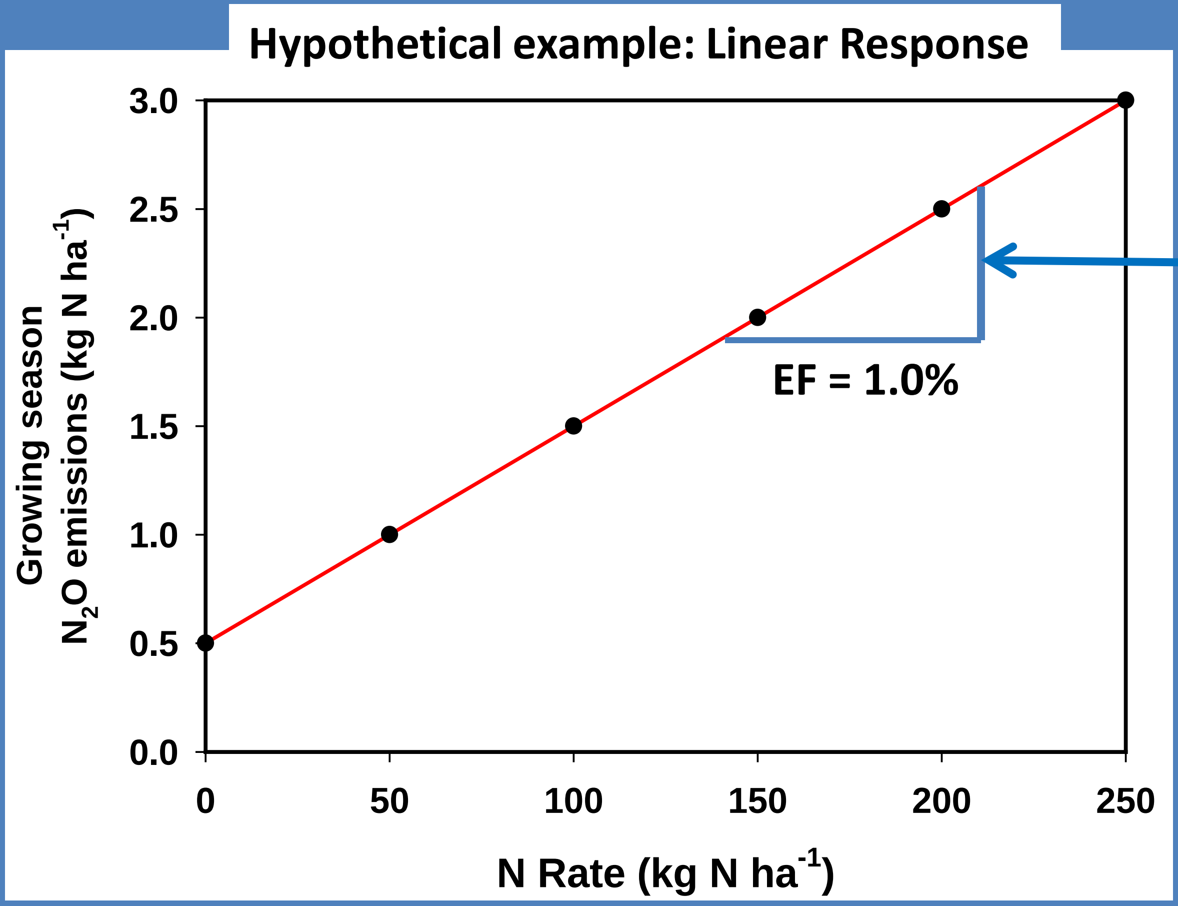
MANAGEMENT EFFECTS ON N_2O EMISSIONS

-Summary of studies in Minnesota (2005 – 2017)

Factor	Treatment Comparison	Sites	Site-years (30)	Reference
N Rate	Varying % of recommended rate	1	4	*2015. Agron. J. 107:337* *2016 J. Environ. Qual. 45:1186*
N source	Conventional Urea vs. Polymer-Coated Urea (PCU)	4	10	*2010 Soil Sci. Soc. Am. J. 74:419* *2011 J. Environ. Qual. 40:1521* *2013 Soil Biol. Biochem. 66:229* *2014 Agron. J. 106:703*
	Conventional Urea vs. Urea amended with microbial inhibitors	3	9	*2011 J. Environ. Qual. 40:1521* *2013 Soil Biol. Biochem. 66:229* *2014 Agron. J. 106:703* *2016 J. Environ. Qual. 45:1186*
N Placement	Banding vs. Broadcast	2	3	*2005 J. Environ. Qual. 34:1467* *2010 Soil Sci. Soc. Am. J. 74:407* *2013 Soil Biol. Biochem. 66:229*
	Deep vs. Shallow	2	4	*2011 J. Environ. Qual. 40:1806* *2014 J. Environ. Qual. 43:1527*
N Timing	Single pre-plant vs. split applications	1	4	*2015. Agron. J. 107:337* *2016 J. Environ. Qual. 45:1186* *2017 J. Environ. Qual. 45:1847*
Tillage	Conventional Tillage vs. Reduced Tillage	2	6	*2005 J. Environ. Qual. 34:1467* *2009 Agri. Ecosys. Environ. 134:234* *2011 J. Environ. Qual. 40:1521*
Rotation	Continuous corn vs. Corn/Soybean	1	5	*2010 Soil Sci. Soc. Am. J. 74:407* *2015. Agron. J. 107:337*
Irrigation	Fully vs. Minimally Irrigated	1	2	*2014 Agron. J. 106:703*
Residue mgmt	Full vs. partial vs. complete removal	1	3	*2014 Bioenergy Res. 7:517*
Drainage	Drained vs. Undrained	1	2	*2017 J. Environ. Qual. 45:1847*

Nitrogen Rate Effects

N Rate: Strongest & most reliable effect on N_2O Emissions:
- Given soil & cropping system, emissions increase with N rate



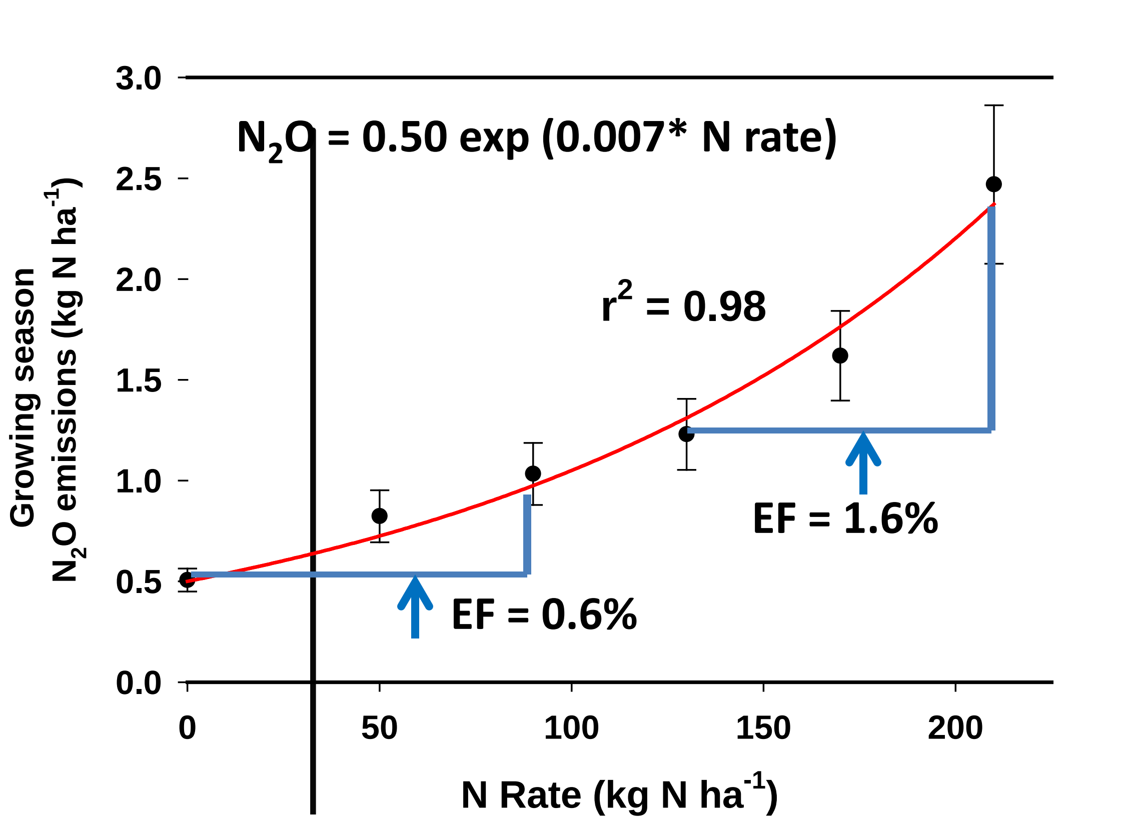
Early studies: Linear response

Emission factor (EF):
- Calculated from slope
- Expressed as % of N applied

Early studies:
- Average EFs: 1%
- Common approximation
- But, EF can vary with:
  - Soil texture
  - Soil organic matter
  - Climate & weather

Nitrogen Rate Effects

Real example: Non-Linear Response



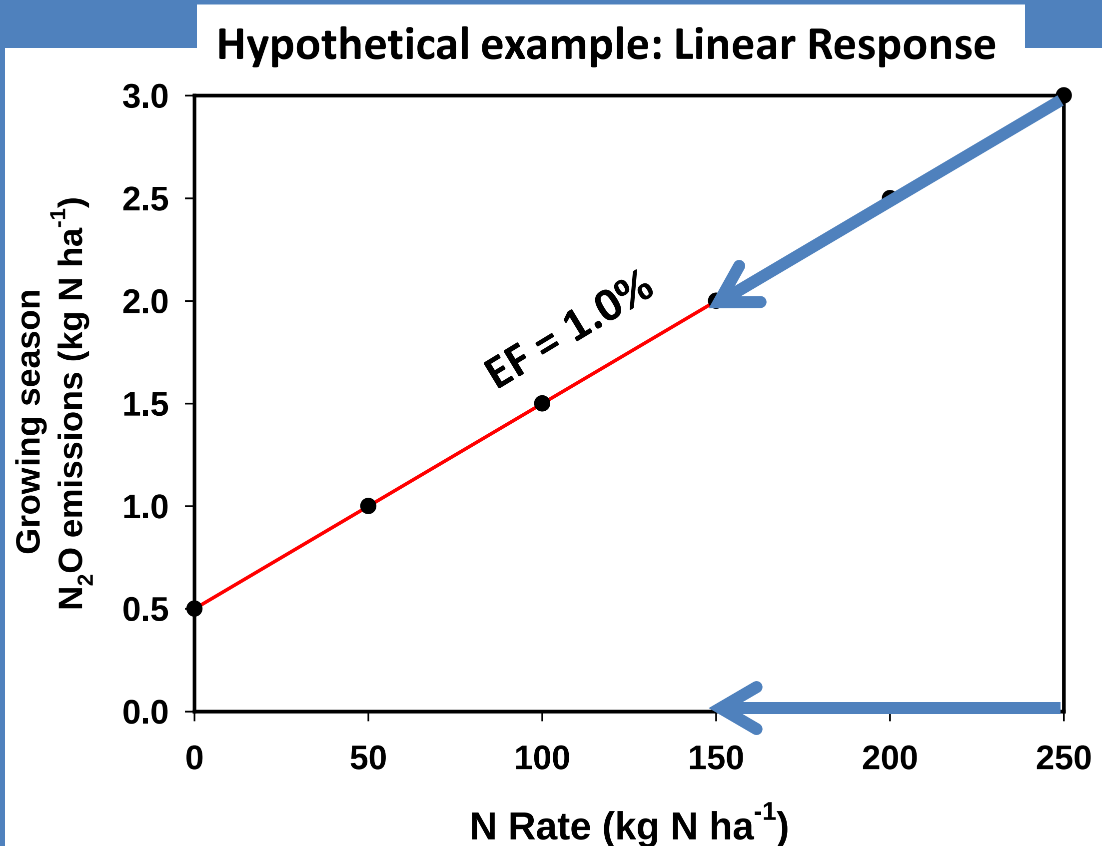
Venterea and Coulter 2015
Waukegan silt loam
Rosemount, MN

Later studies:
- Often a non-linear responses
- EF is not constant
- Increases with N rate

Non-linearity:
- More difficult to estimate N_2O
- Models developed using:

Soil, crop, mgmt, climate inputs

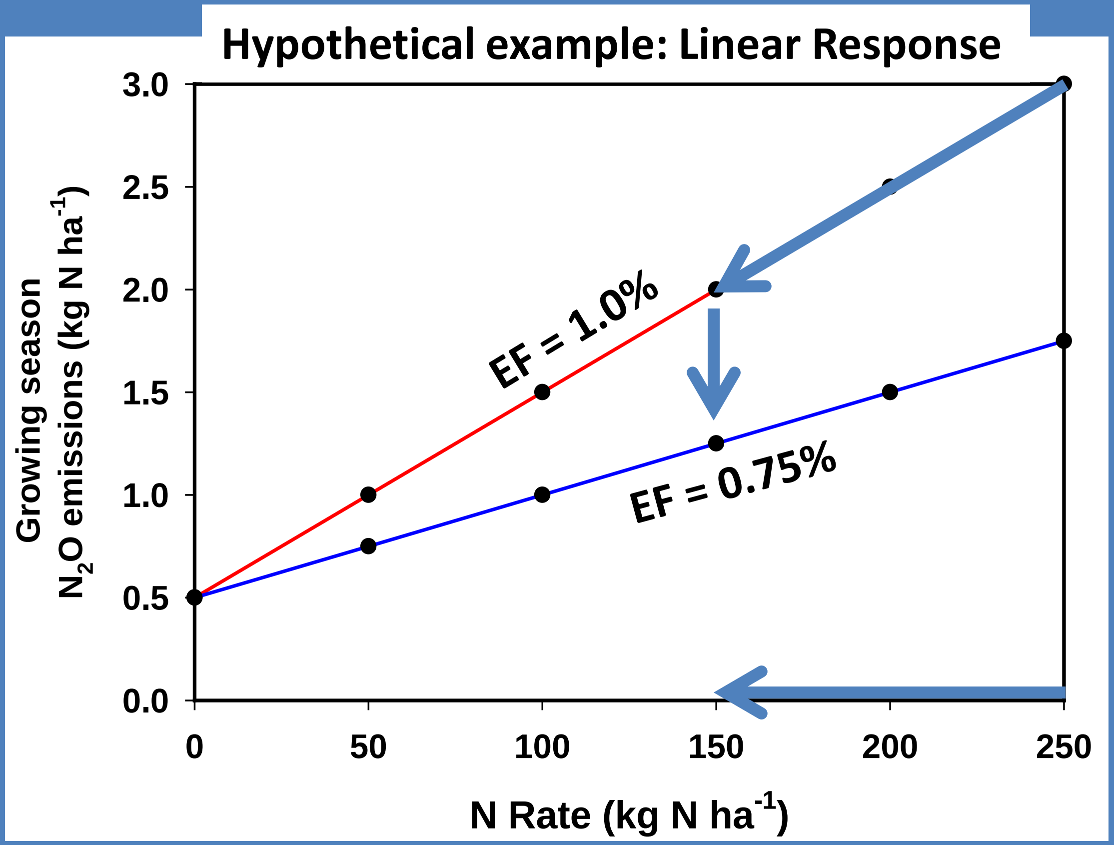
Nitrogen Rate Effects



1st step in trying to manage N_2O:

- Optimize the N rate using available tool & recommendations
- Variable rate / precision methods

Nitrogen Rate Effects



1[st] step in trying to manage N_2O:
- Optimize the N rate using available tool & recommendations
- Variable rate / precision methods

Next step: Use other practices to shift the response curve and decrease the EF:
- Source
- Timing
- Placement
- Other practice

Ultimate goal (win-win):
- Reduce N_2O
- Maintain yield
- At same or lower N rate

Nitrogen Source Effects

Anhydrous ammonia (AA) versus Urea:

AA generally causes greater N_2O emissions than urea when applied at the same rate and time

	<u>% reduction with urea</u>
• **Silt loam soil under varying tillage (*Venterea et al 2005*)**	
•**No till**	**50**
•**Biennial tillage**	**81**
•**Conventional tillage**	**79**
• **Silt loam soil with varying crop rotation (*Venterea et al 2010*)**	
•**Continuous corn**	**57**
•**Corn/soybean**	**50**
• **Loamy sand with varying AA application depth (*Fujinuma et al 2011*)**	
•**Shallow AA injection**	**29**
•**Deep AA injection**	**67**

Nitrogen Source Effects

Anhydrous Ammonia:

- Concentrated N source (82% N)
- Applied in a subsurface band
- High NH_3 concentration in band inhibits second step of nitrification

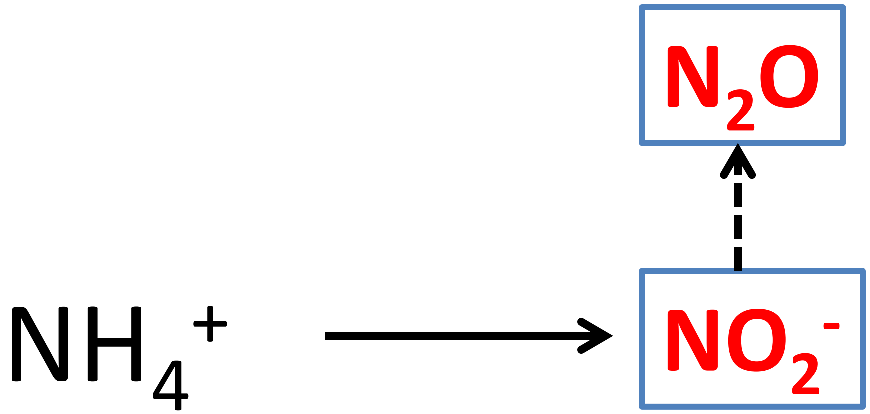
Nitrification usually proceeds rapidly to produce nitrate (NO_3^-) in a two-step process where very little nitrite (NO_2^-) is produced

$$NH_4^+ \longrightarrow NO_2^- \longrightarrow NO_3^-$$

Nitrogen Source Effects

Anhydrous Ammonia:

- Concentrated N source (82% N)
- Applied in a subsurface band
- High NH_3 concentration in band inhibits second step of nitrification



- NH_3 toxicity can stop the process at NO_2^-
- NO_2^- reacts to produce N_2O
- Even if soil is relatively dry

Nitrogen Source Effects

Effects of specialized fertilizer products and additives:

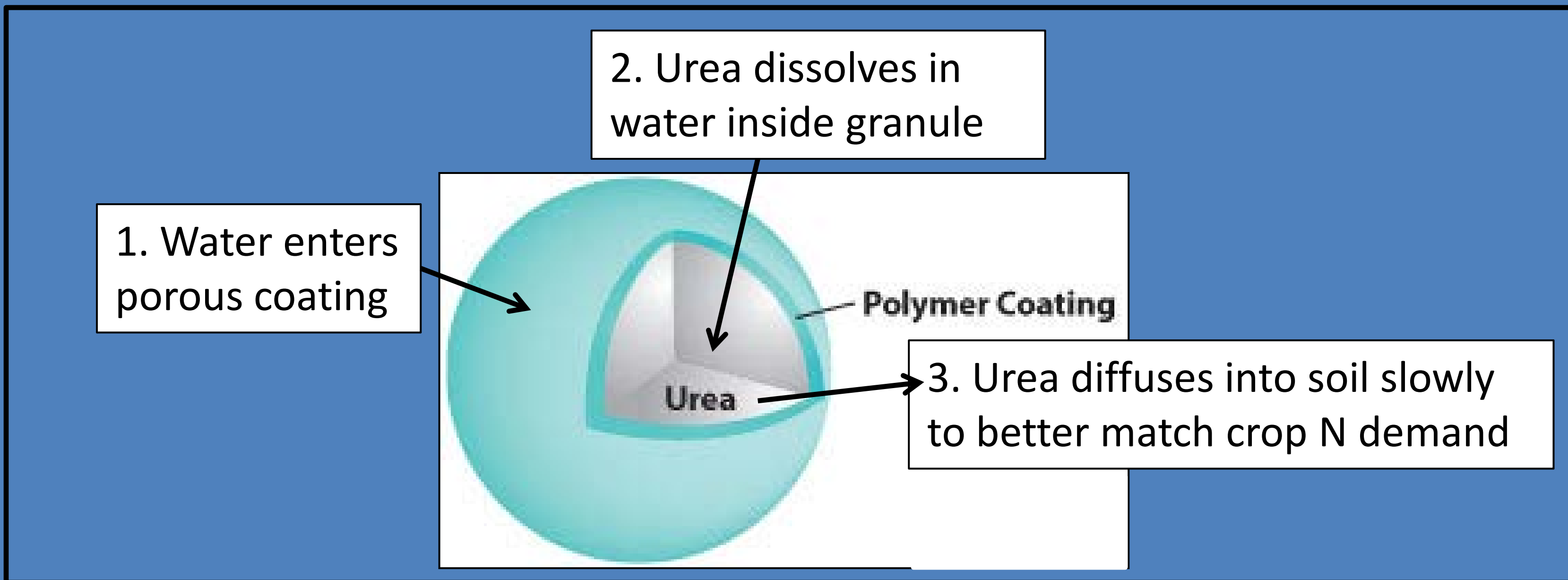
1. **Coated urea products**
   Designed to slow down N release physically

2. **Microbial inhibitors**
   Designed to slow down specific microbial processes

   - **Urease inhibitors**

   - **Nitrification inhibitors**

Polymer-Coated Urea (PCU)



In irrigated systems: Reliable reductions in N_2O (up to 70%)

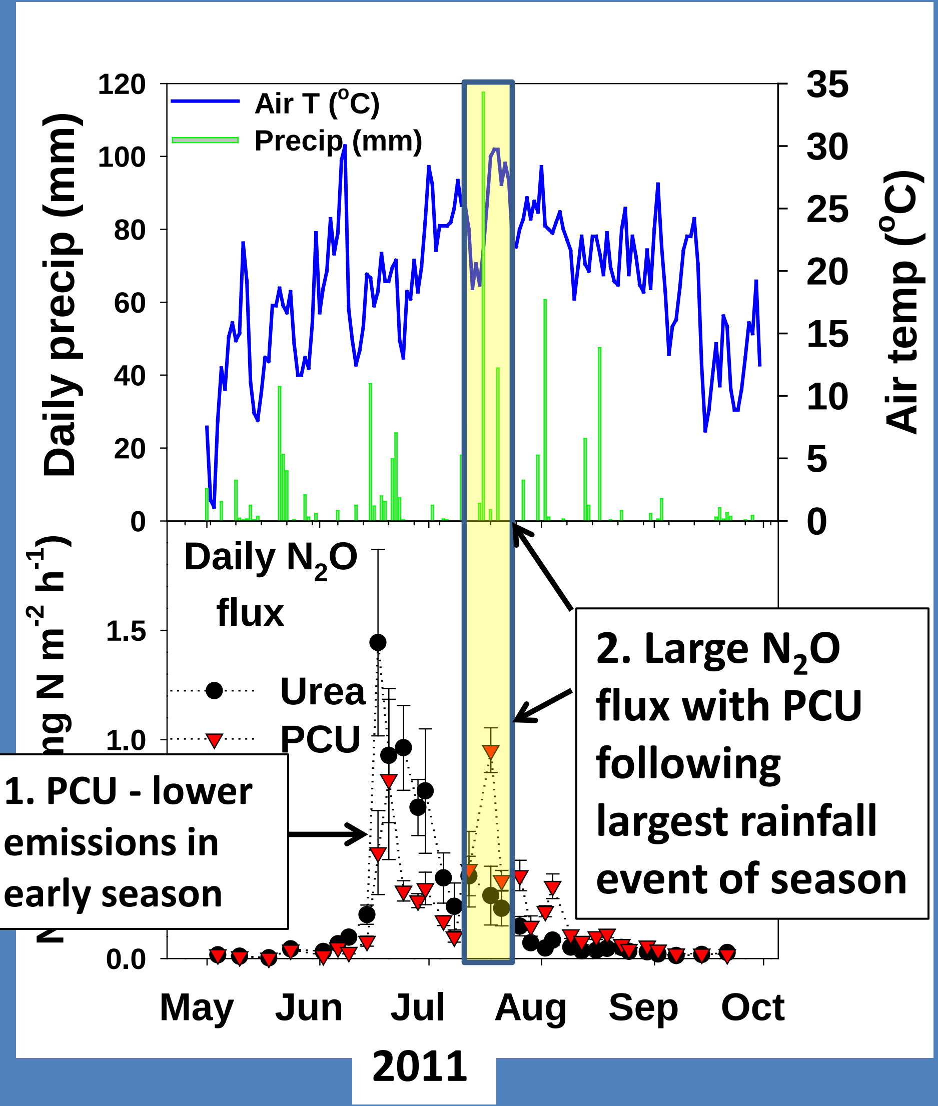
Delgado and Mosier (1996); Shoji et al. (2001); Halvorson et al. (2010, 2011, 2013)

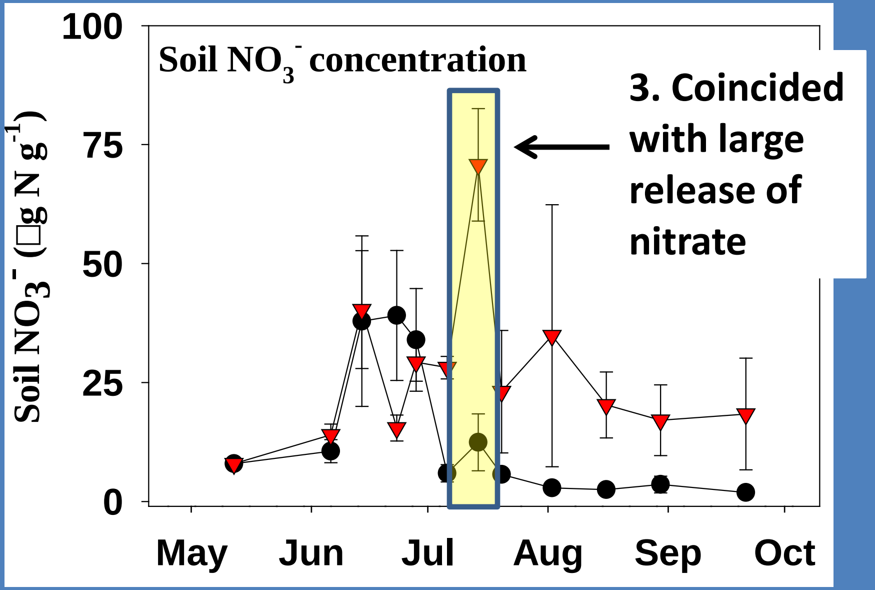
In rainfed systems: Not as reliable for reducing N_2O

Missouri: Nash et al. (2012)
Kentucky: Sistani et al. (2011)
Minnesota: Venterea et al. (2011); Maharjan et al. (2013)
Brazil: Soares et al. (2015)

Polymer-Coated Urea (PCU) vs. Urea

Both sources applied prior to planting

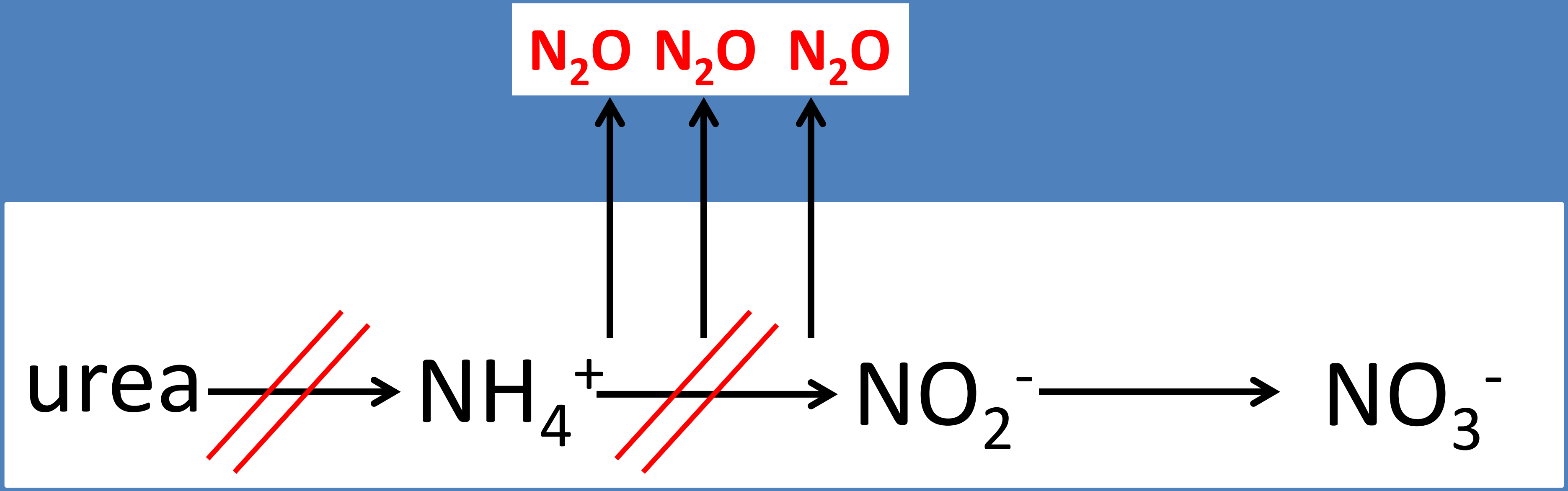




- N release from PCUs responds mainly to weather and not necessarily in synch with crop N demand
- Not always reliable for N_2O reduction

Maharjan & Venterea (2013)
Waukegan silt loam, St. Paul

Microbial Inhibitors



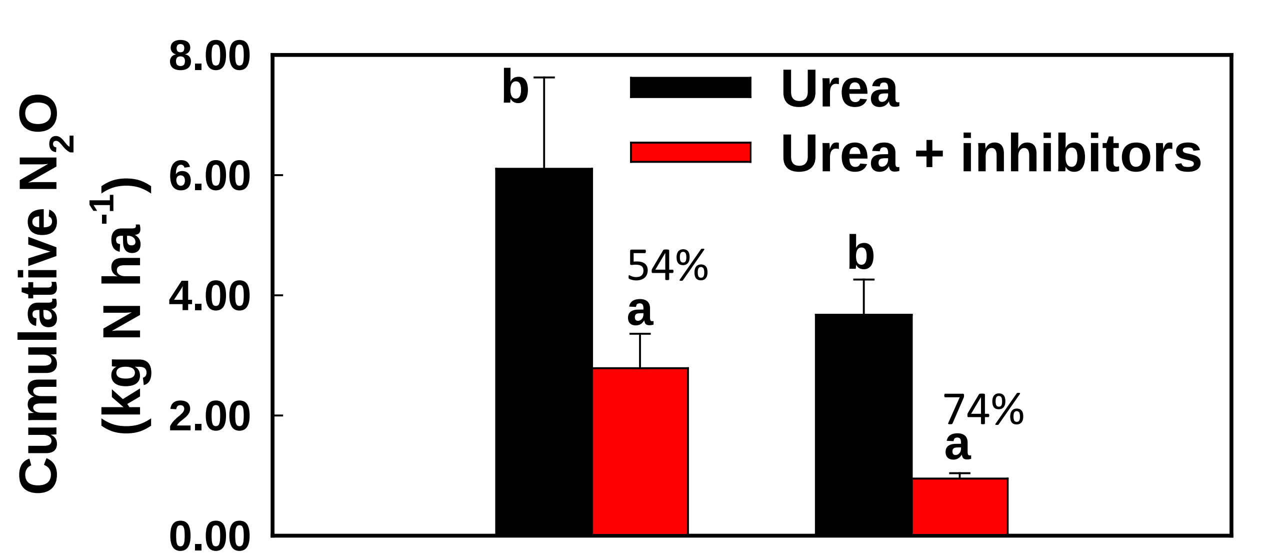
1. Urease inhibitors (e.g. NBPT) inhibit urea hydrolysis

2. Nitrification inhibitors (e.g. nitrapyrin, DCD, others) inhibit the first step of nitrification, oxidation of NH_4^+

Both inhibitors designed to increase opportunity for plant to utilize soil N before it is processed by microbes

Microbial Inhibitors

- **Inhibitors: More reliable than PCUs in several studies:**
  - **Minnesota:** ***Maharjan et al. 2014; Maharjan & Venterea 2013***
  - **Brazil (sugar cane):** ***Soares et al. 2015***



Precipitation	2011	2012
20 June thru 1 Oct	471 mm	174 mm

- **Inhibitors (combination) effective both years**
- **PCU only effective in dry year (2012)**

Maharjan & Venterea (2013)
Waukegan silt loam, St. Paul

Microbial Inhibitors

Limitations:

- **Inhibitors not always reliable**
  - **(e.g. *Parkin & Hatfield, 2010, Venterea et al. 2011*)**
- **Nitrification and urease inhibitors have limited duration of effectiveness**
- **Inhibitor chemicals decompose in soil**
- **Decomposition rate increases with temperature**

Fertilizer Placement Effects

1. Depth (of incorporation or injection)
2. Broadcast vs. Banding

1. Depth – Inconsistent results across studies

Deeper placement:

→ Higher soil moisture – tends to increase denitrification
But can also result in more N_2O being fully reduced to N_2

→ Lower soil organic matter – tends to decrease denitrification

Fujinuma et al 2011: Shallow (4-in) AA increased N_2O by 100% compared to conventional depth (8 in)

Maharjan & Venterea 2015: No effect of AA application depth

Fertilizer Placement Effects

2. Broadcast vs. Banding (Urea)

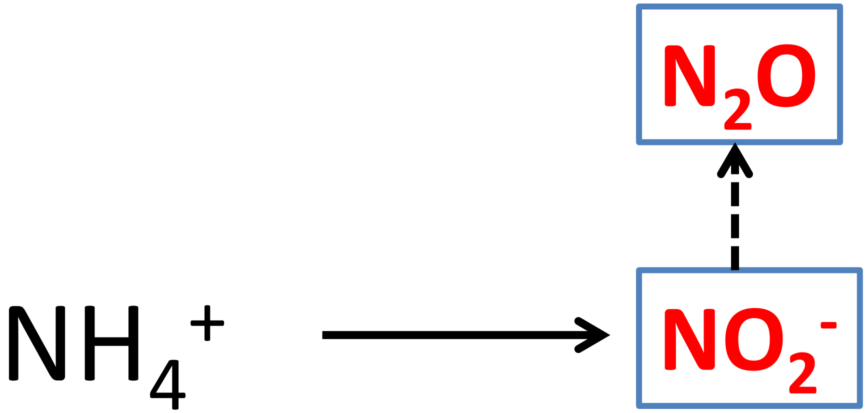
Banding increased N_2O emissions compared to uniform broadcast:

- Montana: *Engel et al. (2010)*
- Colorado: *Halvorson & Del Grosso (2013)*
- Minnesota: *Maharjan & Venterea (2013)*

Banding urea has effects similar to Anhydrous Ammonia:

High NH_3 concentration in band inhibits the second step of nitrification

Maharjan & Venterea (2013), Venterea et al. (2015)



- NH_3 toxicity can stop the process at NO_2^-
- NO_2^- reacts to produce N_2O
- Even if soil is relatively dry

Nitrogen Fertilizer Application Timing

General Assumption: Improved synchrony between N application timing and crop N demand will reduce N losses

1. **Spring vs. Fall application should reduce N_2O**

Not always the case:
Hernandez-Ramirez et al. 2009*; *Tenuta et al., 2016

2. **Late vs. Early season application should reduce N_2O**

Often not the case

Improved timing of N application often does not reduce N_2O:

Burton et al. (2008) New Brunswick - potato

Split application reduced N_2O in only one of two years

Zebarth et al. (2008) New Brunswick - corn

No effect of early vs. late spring application

Phillips et al. (2009) North Dakota - corn

Trend (P=0.103) for greater emissions with late vs. early spring application to corn

Zebarth et al. (2012) New Brunswick – potato

No effect of single vs. split application to potato

Allen et al. (2012) Australia – sugar cane

Split application reduced N_2O with 200 kg N ha^{-1} but not with 100 kg N ha^{-1}

Drury et al. (2012) Ontario – corn

Split application reduced N_2O in CT system but not in NT or ZT systems

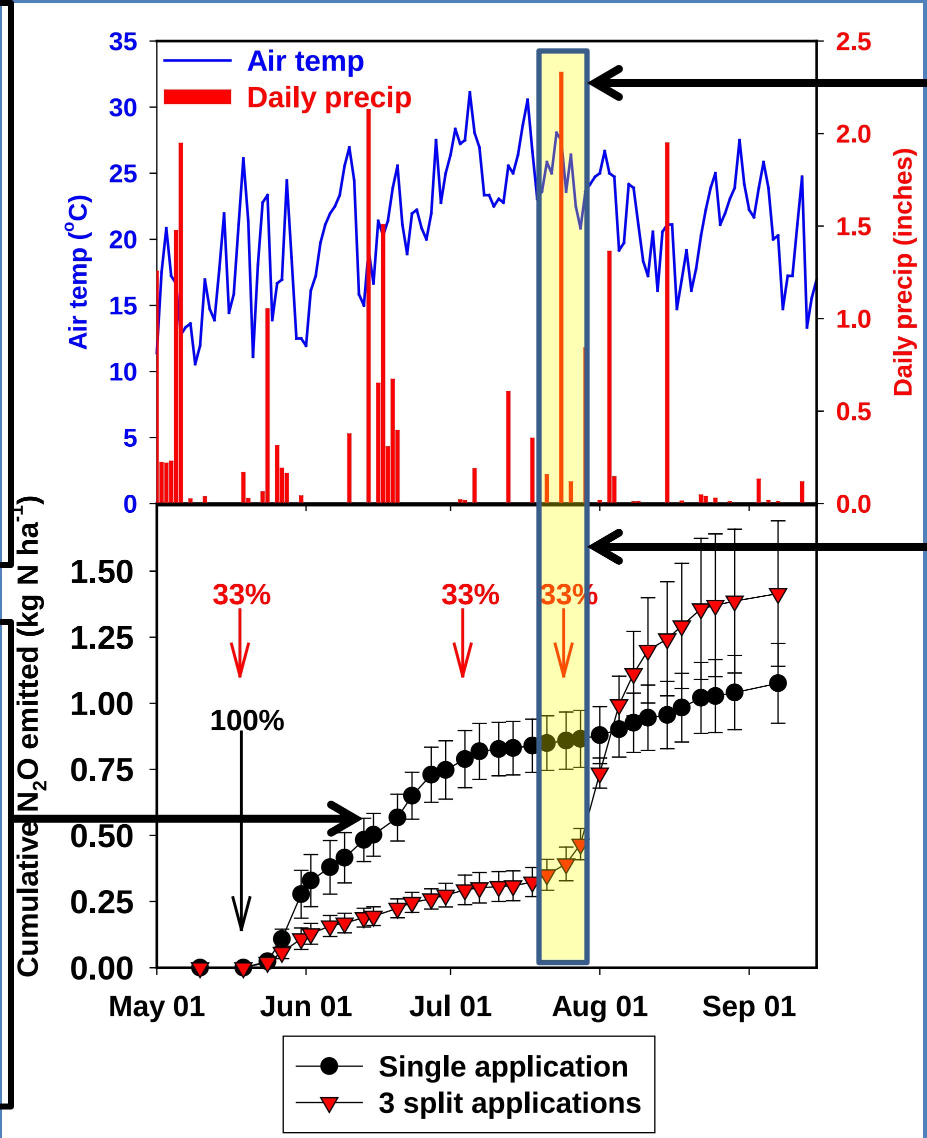
Venterea and Coulter (2015) Minnesota - corn

Split application increased N_2O in one of two growing seasons

Nitrogen Fertilizer Application Timing

3. Total emissions greater with split application across all five N rates, and both rotations (C/C and C/S)

1. Single application had greater cumulative N_2O emissions early in season



2. Large flux occurred following 3rd split application, after largest rainfall event of season

4. In second year, no effect of application timing

Venterea and Coulter (2015) Minnesota Waukegan silt loam, Rosemount

Challenges of reducing N_2O emissions

2. Large N_2O fluxes can occur even when the crop is present and well-developed

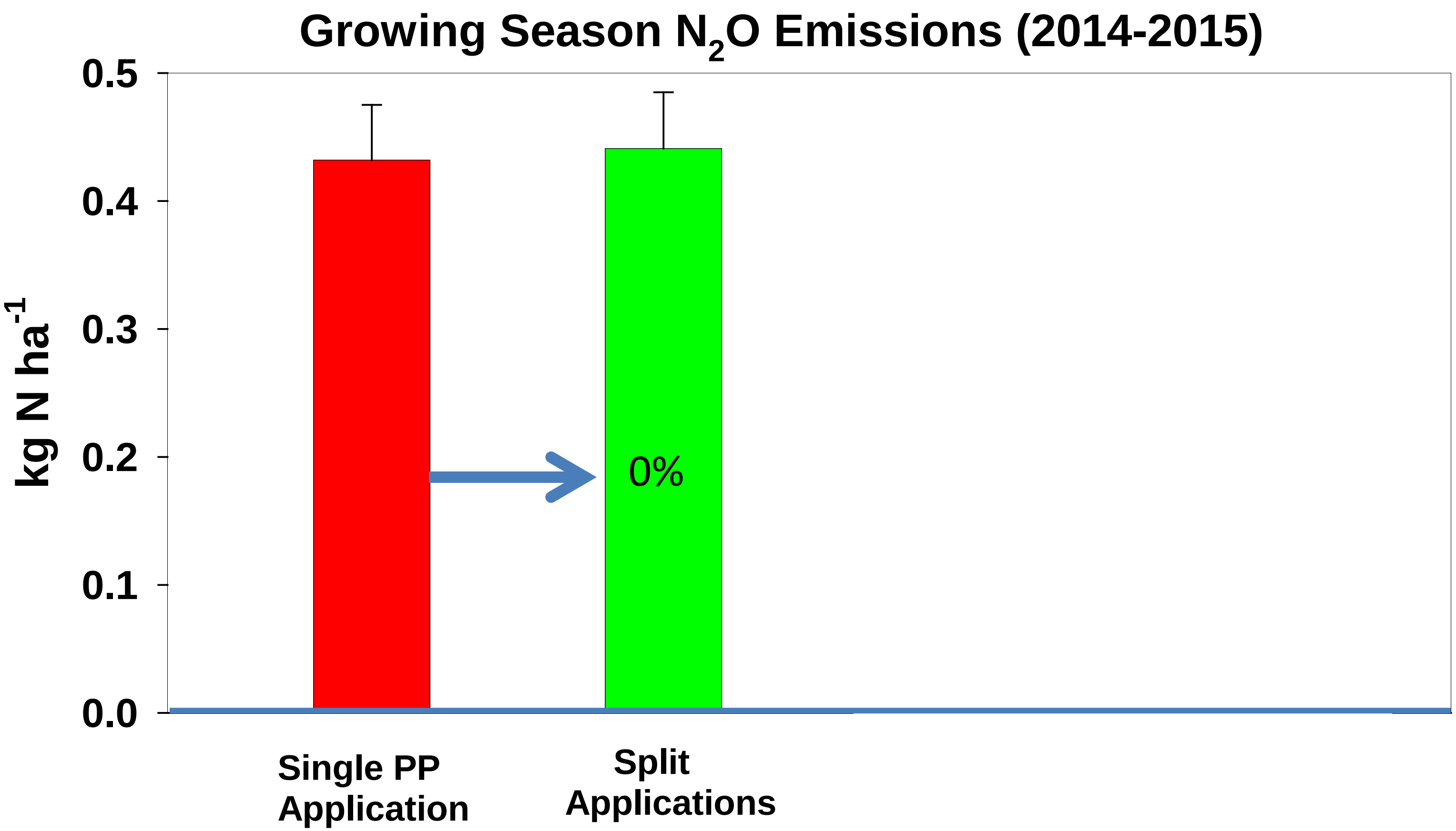
-Soil biochemical reactions are very fast

-Diffusion of N_2O gas is very fast

-Higher temperatures later in season further speed up soil biochemical processes and diffusion

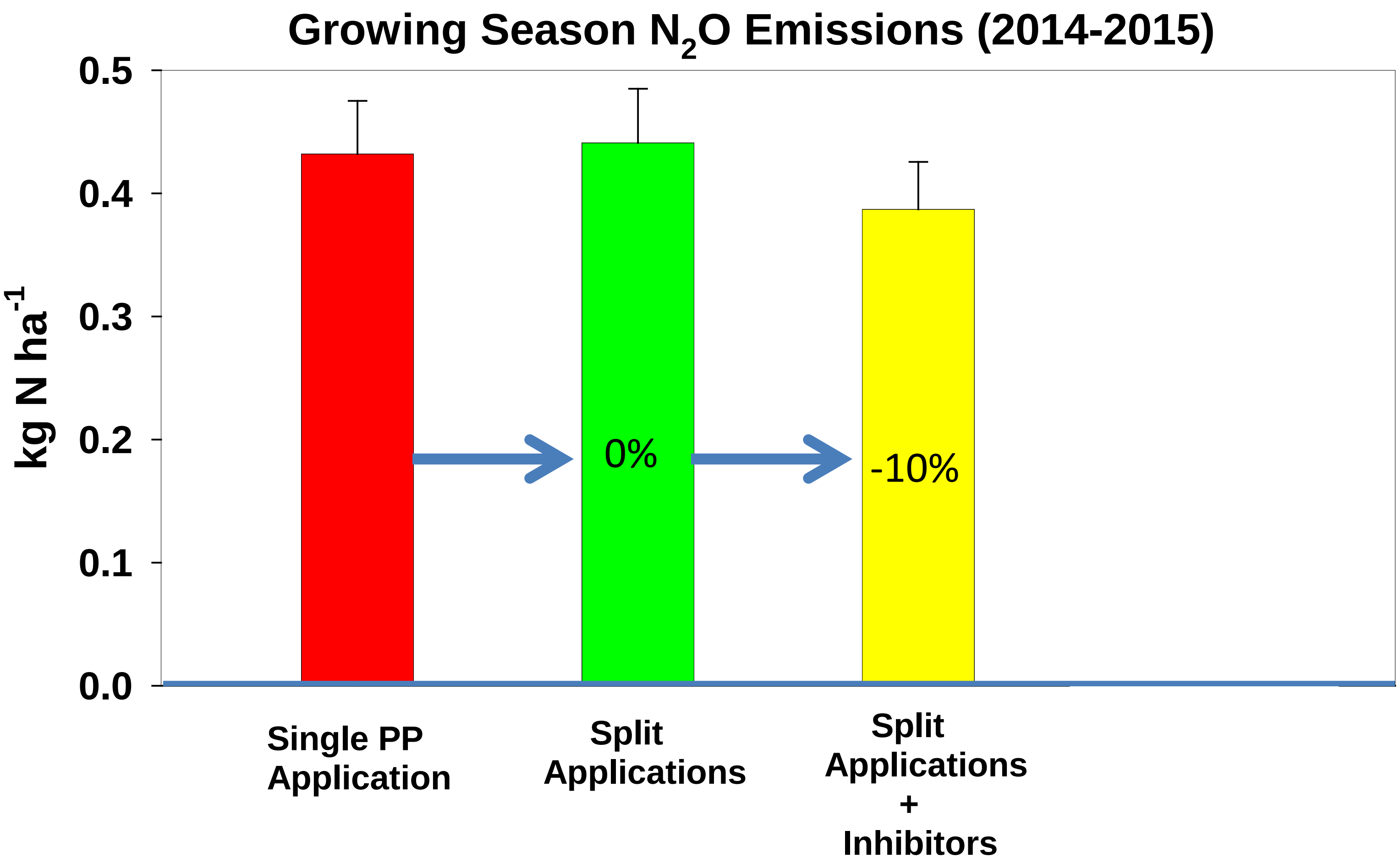
-Large precip events + warm temps → large fluxes

Adjusting timing by itself: Not always reliable
Timing + other practices: May be more reliable



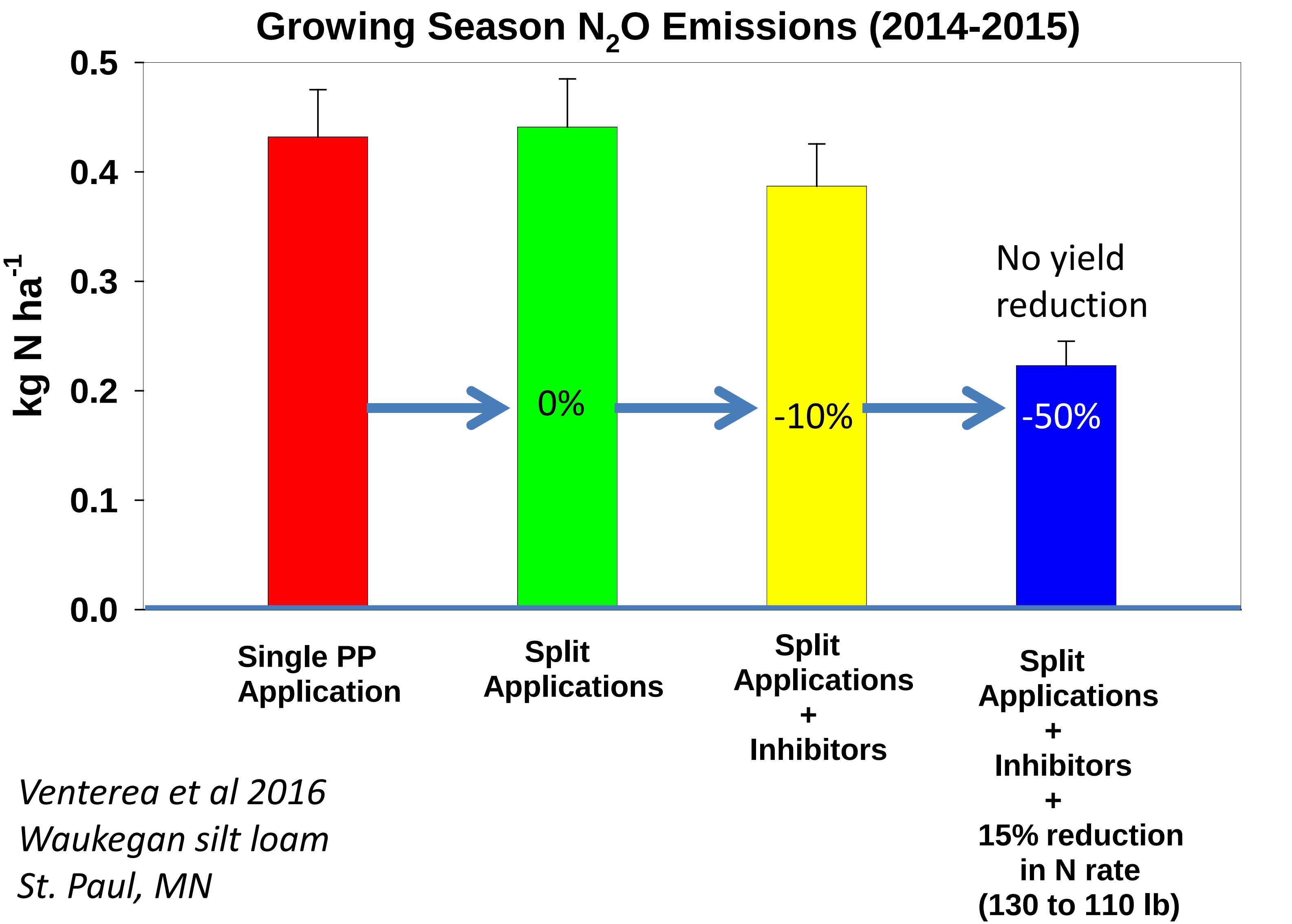
Venterea et al 2016
Waukegan silt loam
St. Paul, MN

Adjusting timing by itself: Not always reliable
Timing + other practices: May be more reliable



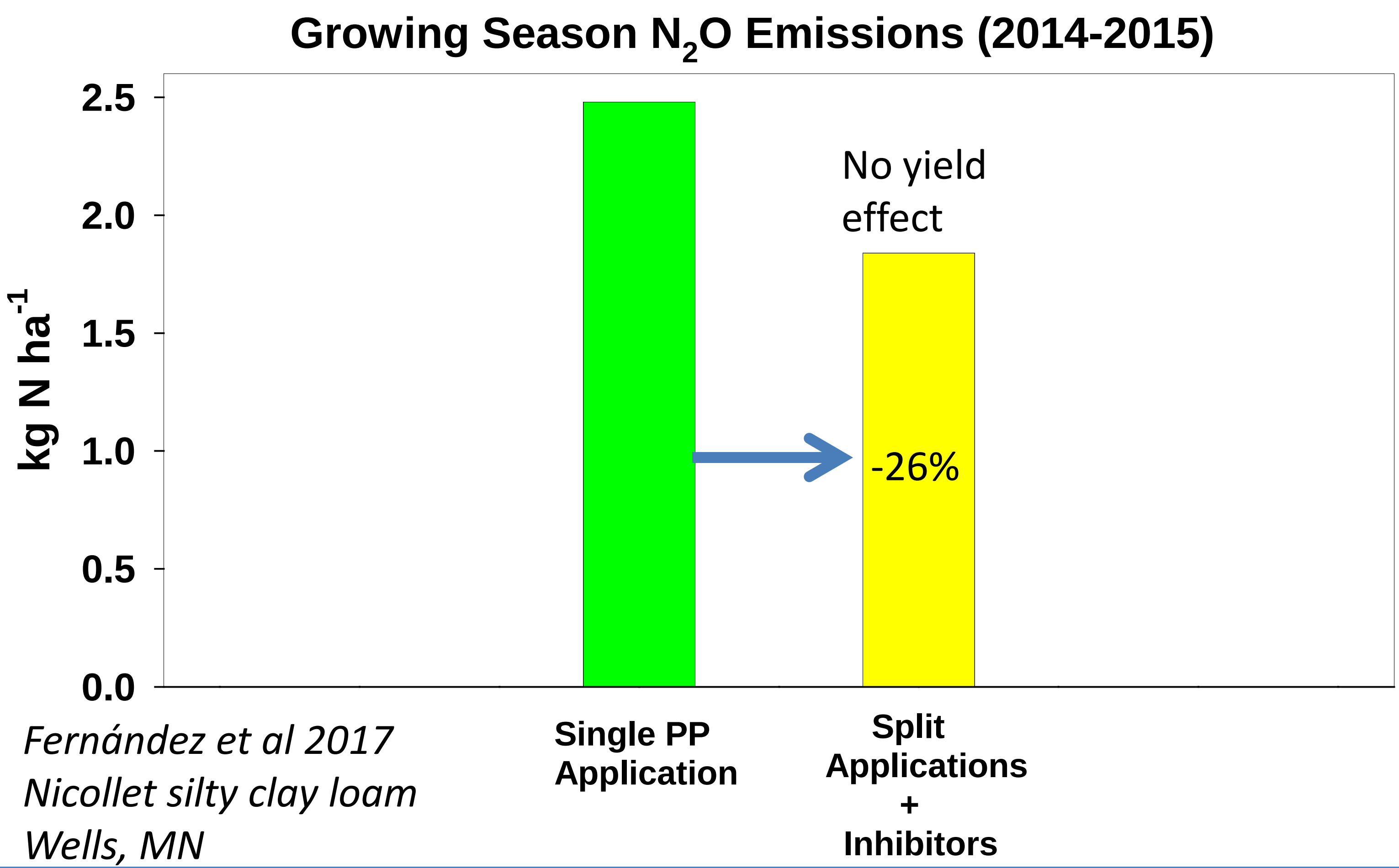
Venterea et al 2016
Waukegan silt loam
St. Paul, MN

Adjusting timing by itself: Not always reliable
Timing + other practices: May be more reliable



Venterea et al 2016
Waukegan silt loam
St. Paul, MN

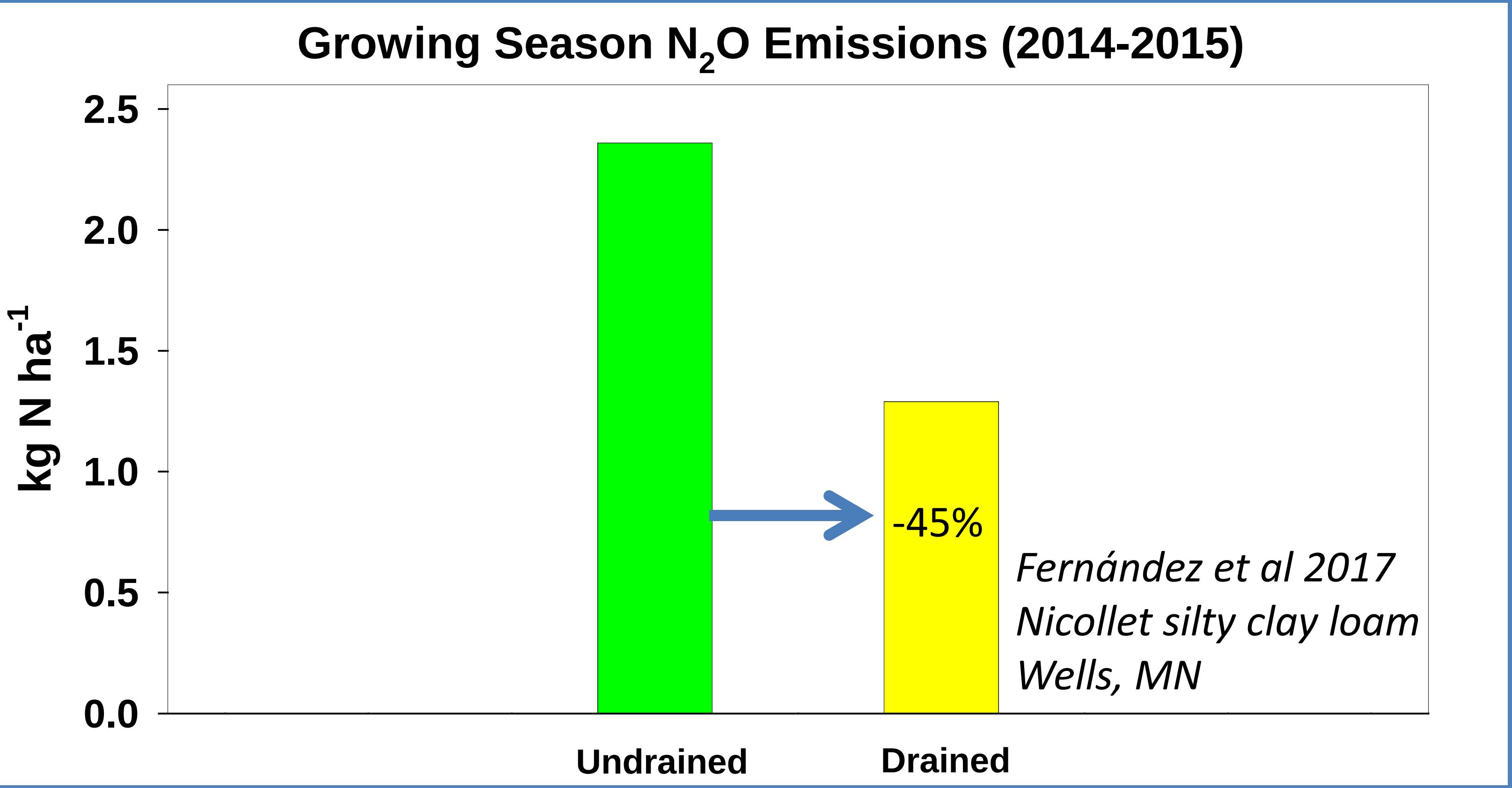
Adjusting timing by itself: Not always reliable
Timing + other practices: May be more reliable



Fernández et al 2017
Nicollet silty clay loam
Wells, MN

Practices other than the 4Rs

- Tillage
- Rotation
- Residue mgmt
- Irrigation
- Drainage → Surprisingly few studies

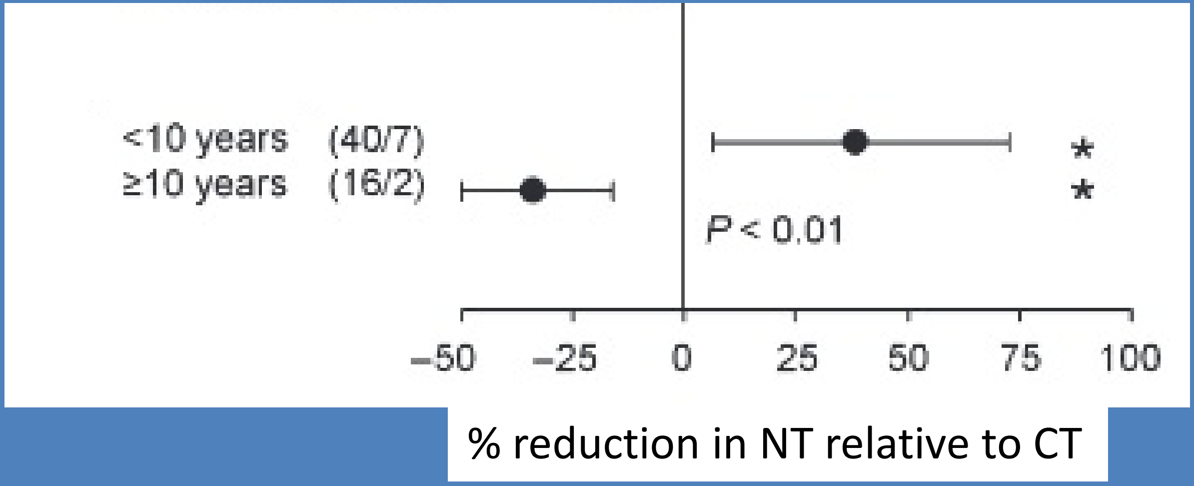


Tillage Effects on N_2O Emissions

Many individual studies, but conflicting

Global Meta-analysis - *Van Kessel et al. 2013.* Effects depend on:

- Climate regime
- Duration of adoption
- Interactions with N mgmt practices



Strongest effect

- *N_2O __Increased__* in NT relative to CT - when NT practiced for < 10 years
- *N_2O __Decreased__* in NT relative to CT - when NT practiced for 10 years or more
- Reasons for this change over time not fully understood

Managing N_2O Emissions: Concluding Remarks

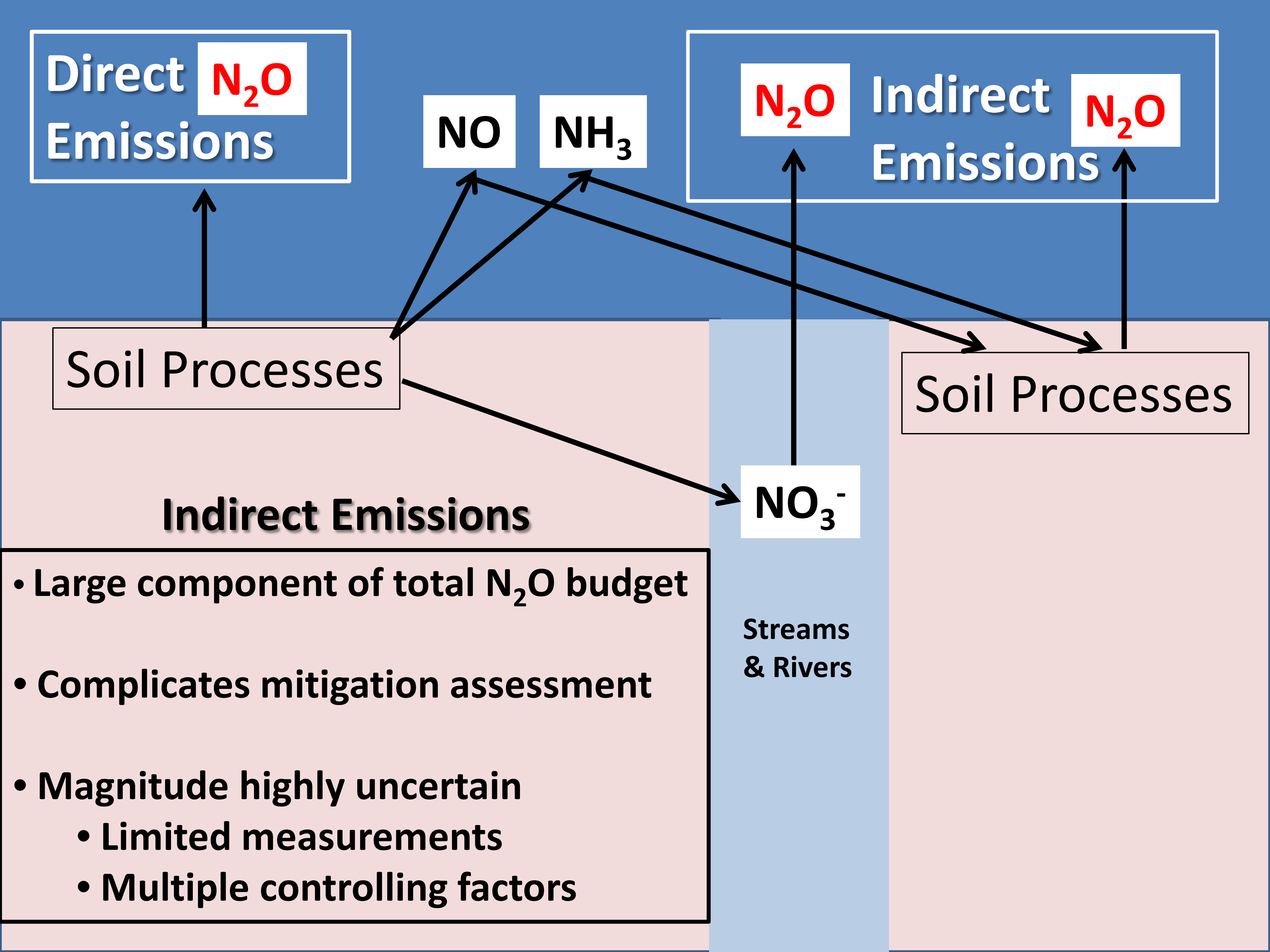
- Any practice that allows for N rate reduction:
  - Likely to result in disproportionately large decrease in N_2O emissions

- Microbial inhibitors proven to be reliable:
  - Need for new products:
    - Longer lifetime in soil
    - To target specific N_2O producing reactions and enzymes

- Modified timing by itself not reliable for reducing N_2O losses:
  - Combining with inhibitors and/or N rate reduction are recommended

- Banded N fertilizers high risk for high N_2O losses:
  - Inhibitors recommended for any banded application (urea or AA)

- Better understanding of basic biochemical controls over N_2O-producing processes needed to develop effective mitigation methods


Direct N_2O Emissions
NO
NH_3
N_2O
Indirect Emissions
N_2O
Soil Processes
Soil Processes
NO_3^-
Indirect Emissions
• Large component of total N_2O budget
• Complicates mitigation assessment
• Magnitude highly uncertain
• Limited measurements
• Multiple controlling factors
Streams & Rivers

Indirect N_2O Emissions Complicate Assessment of Mitigation Effects

Urea decreases N_2O emissions compared to AA:

-However, Urea *increased* NO emissions compared to AA

(Fujinuma et al., 2011)

Broadcasting appl. decreases N_2O compared to banding

-However, broadcasting can *increase* NH_3 losses

(Maharjan & Venterea, 2013 and unpublished)

Drainage decreases N_2O emissions compared to no drainage

-However, drainage could *increase* NO_3^- leaching

Indirect N_2O Emissions

Critical question:

How much (what fraction) of the NO / NH_3 / NO_3^- released into the environment is eventually converted to N_2O?

- **Simplistic assumptions used to estimate this fraction**

  1. **Fixed % of the N converted to N_2O (% are based on small number of studies)**

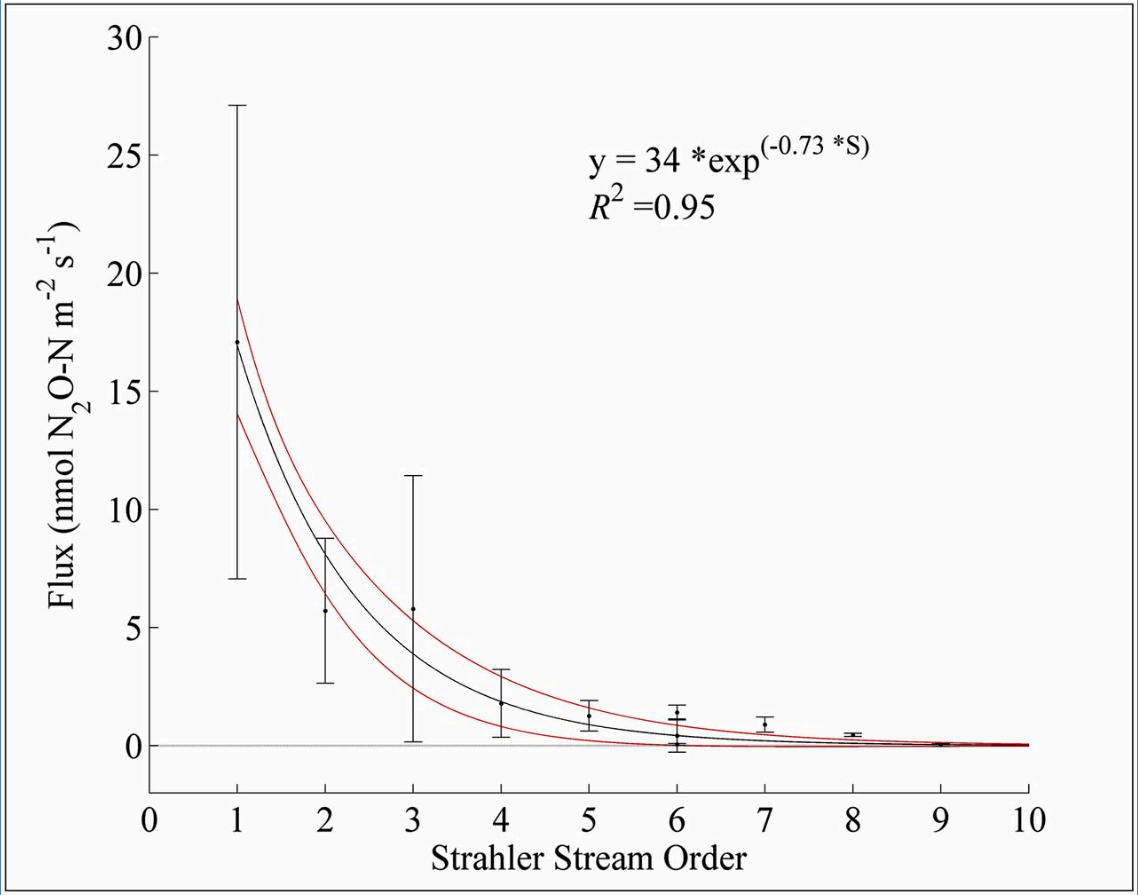
  2. **The % converted to N_2O is independent of the characteristics of the receiving ecosystem**

Indirect N_2O Emissions

Recent study in Minnesota (Turner et al. 2015)

- Aquatic N_2O emissions: floating chambers and a canoe
- Fluxes depended on location of streams and rivers within the landscape

N_2O flux versus Strahler stream order



Fluxes:

- Greatest in smaller, lower order streams
- Exponential decrease with stream order
- Suggested aquatic emissions greater than previously estimated

Indirect N_2O Emissions

- **Any practice that reduces N losses from the field in any form (NH_3, NO, NO_3) will reduce indirect N_2O emissions**

- **Efforts to improve water quality expected to significantly reduce indirect N_2O emissions**

- **Magnitude of N_2O mitigation effects highly uncertain:**

- **More studies needed to quantify the fraction of leached N that is converted to N_2O in receiving aquatic systems**